THE DETERMINATION AND NATURE OF THE LYOTROPIC LIQUID CRYSTALLINE PHASE TRANSITIONS IN THE AMMONIUM PENTADECAFLUOROOCTANOATE DEUTERIUM OXIDE SYSTEM.

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ABSTRACT

The work presented in this thesis is the first stage in an investigation into the role of the counter-ion in determining phase behaviour. Specifically a high resolution phase diagram of the system ammonium pentadecafluorooctanoate/heavy water has been obtained and compared with that of the system caesium pentadecafluorooctanoate/heavy water. Three physical techniques were used, namely; deuterium NMR spectroscopy, differential scanning calorimetry and conductivity measurements. The main method used for phase transition identification was deuterium NMR spectroscopy and therefore a detailed NMR theory section is included.

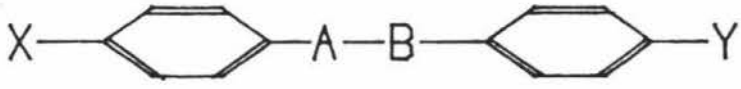
Experimental evidence indicates no difference in the nature of the mesophases for the different counter-ion systems studied. There is, however, a difference in the temperatures and compositions at which the phase transitions occur in the two systems. These differences are interpreted in terms of differences in the solubilities of the salts and the hydration energies of the counterions.

INTRODUCTION

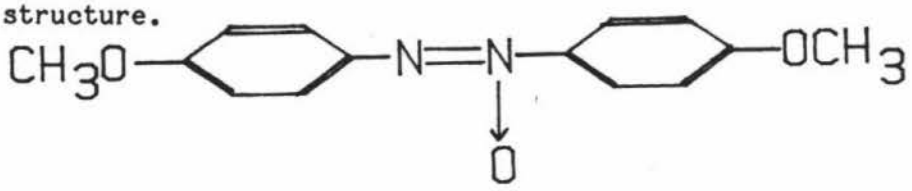
In 1890,O Lehmann [1] first used the term liquid crystal to descibe the states of matter intermediate to crystalline solid and normal (isotropic) liquid phases, which due to their milky appearance were originally thought of as being impure solutions. Many thousands of organic compounds exhibit liquid crystalline behaviour above their melting points, and these liquid crystals have since been referred to as the fourth state of matter. Liquid crystals fall into two main classes - Thermotropic and Lyotropic.

Thermotropic Liquid Crystals

The name thermotropic derives from the fact that the main factor determining the phase is the temperature. Thermotropics are usually large organic molecules with various functional groups such as azobenzenes,azoxybenzenes,nitrones and numerous others. The vast majority have the structure



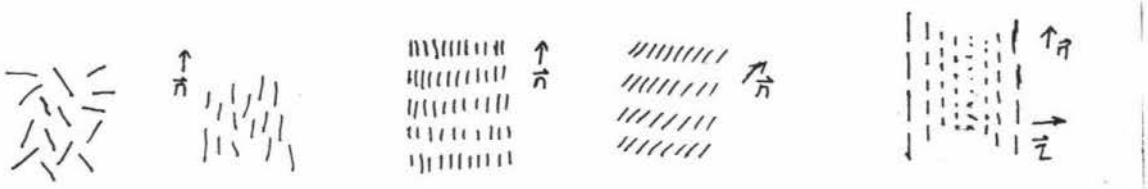
and possess two or more aromatic rings,one or more bridging groups,A-B,that bind the rings together,and two terminal groups X and Y usually on the long axis of the molecule. X and Y are often the same group. An example of a thermotropic liquid crystal is p-azoxybenzene which has the structure.



Thermotropics are single component systems or mixtures of similar types of molecules. For example 4-Methoxy-4'-n-butyl-benzylideneaniline (MBBA) is an important room temperature nematic liquid crystal whose liquid crystalline temperature range can be increased by the addition

of 4-ethoxy-4'-n-butyl-benzylideneaniline (EBBA)[2].

There are three basic types of thermotropic liquid crystalline mesophases [3]:smectic,from the Greek for greasy;nematic,from the Greek for threads; and cholesteric so called because it is mostly formed by cholesteryl derivatives (but not cholestertol itself). A schematic representation of the ordering of the symmetry axes of the molecules in each of these phases is given below.



isotropic nematic smectic A smectic C cholesteric

There are many types of smectic liquid crystals that have been given the designation of smectic A,B,C...etc [4]. Smectic liquid crystals have a layered structure with the centres of gravity of the elongated molecules arranged in equidistant planes. The long axes of the molecules are parallel to a prefered direction, known as the director $\vec{n}$,which may be normal to the planes (smectic A) or tilted to a certain angle for example (smectic C).

Nematic liquid crystals have long range orientational order of the long molecular axes but no long range translational order. Nematics are important technologically because they can be aligned such that the orientational order can be extended over the whole of a macroscopic sample by either a magnetic field or an electric field. Use of the latter is made in Liquid Crystal Displays (LCD's). A simple LCD consists of two glass plates coated on the inside surface with a transparent electrode layer between which a liquid crystal has been

sandwiched.

Cholesteric liquid crystalline mesophases can be thought of as being a twisted nematic structure where the molecules are aligned parallel to a prefered direction ,$\vec{n}$. The molecules that make up a cholesteric mesophase are usually flat and lie together in planes. The mesophase is made up of layers of these planes with each of the planes being rotated slightly about an axis perpendicular to the planes. When proceeding normal to the plane $\vec{n}$ rotates continuously giving a helical type structure the axis of which is given by another vector quantity ,$\vec{z}$. The pitch ,P, is the proportion of 2π necessary to rotate $\vec{n}$ when proceeding along $\vec{z}$ or in other words the angle that each plane has been rotated relative to the previous plane. Certain cholesteric liquid crystals exhibit colour changes over the entire colour scale from red to violet when a variable such as temperature is changed. This gives rise to applications such as skin temperature measurement for the diagnosis of tumours and vascular disease and for monitoring skin grafts.

Recently another type of thermotropic phase has been discovered which is made up of flat disc shaped molecules [5]. These molecules have their symmetry axes perpendicular to the plane of each disc and tend to form a hexagonal columnar phases in which the molecules are stacked on top of each other. The sequence of phase transitions is columnar to nematic to isotropic.

Lyotropic Liquid Crystals

Lyotropic liquid crystals are formed on mixing two or more components. One of these components must be an amphiphile,a molecule which contains

a polar head group (usually ionic) and one or more long hydrophobic chains,and one of the other components in the system must be a solvent (usually water). Lyotropic liquid crystals occur in all living systems. Examples of this are cell membranes which are liquid crystals made up of bilayers of phospholipids. Man made lyotropic liquid crystals can be traced as far back as Ancient Rome when a primitive form of soap was used which when mixed with water gave the first artificially produced liquid crystalline mesophase [6]. In spite of this,very little quantitative work has been undertaken on these systems and our knowledge is very primitive.

Most of the work done until fairly recently has been qualitative and has been undertaken on the behalf of soap and detergent manufacturers. This work was not particularly detailed and was aimed at ensuring that the soap remained in an easy to handle low viscosity phase rather than a more troublesome high viscosity phase. Phases were identified and labelled by names such as neat soap,middle soap and isotropic phase.

The dissolution of an amphiphile in water gives micelles at low concentrations and liquid crystals (lyotropic amphiphillic mesophases) at higher ones. Critical micelle concentrations (c.m.c.) are typically 10^{-3} to 10^{-1} mol dm^{-3} whilst `critical' liquid crystal concentrations can be as low as 0.5 mol dm^{-3}. In micellar solutions the amphiphilic aggregates are of finite size (small spheres , rods or discs), whilst in mesophases they have traditionally been envisaged as being of indefinite size (cylinders or bimolecular layers)[7]. For mainly this reason studies of micellar solutions,on the one hand, and mesophases,on the other,have developed into separate domains of

endeavour. The relatively recent discovery of nematic mesophases [8] and the results of subsequent investigations of their structures and properties clearly indicate,however,that our fundamental understanding of liquid crystal mesophases cannot be diverted from that of micellar solutions.

Nematic mesophases are micellar solutions in which there is long range orientational ordering of the symmetry axes of the micelles. Nematic phases consisting of discoid (oblate ellipsoids or discs) micelles (N_D) tend to occur intermediate to lamellar phases and isotropic micellar solutions,whilst ones consisting of calamitic (prolate ellipsoids or rods) micelles (N_C) occur intermediate to hexagonal phases and isotropic micellar solutions [9]. In terms of their symmetry properties, the former can be compared with the thermotropic smectic A to nematic to isotropic liquid sequence of phases exhibited by calamitic molecules and the latter to the thermotropic columnar to nematic to isotropic liquid sequence exhibited by discoid molecules. It is not unreasonable, therefore, to expect that phase transitions in lyotropic systems can be understood in terms of the theories developed for thermotropic systems. But it is not necessarily so because the two kinds of system are fundamentally different from each other in one important aspect. In lyotropic systems the mesogenic particles are amphiphilic aggregates whose detailed structures vary with the thermodynamic state (i.e temperature, pressure, composition, and mesophase structures) whilst in thermotropic systems the structure of the particles is an invariant property (except for internal conformational changes). Phenomenological theories have been developed which attempt to relate the detailed molecular organisation of the

aggregates to the molecular and inter-aggregate interactions, but these are, at best, primitive [10].

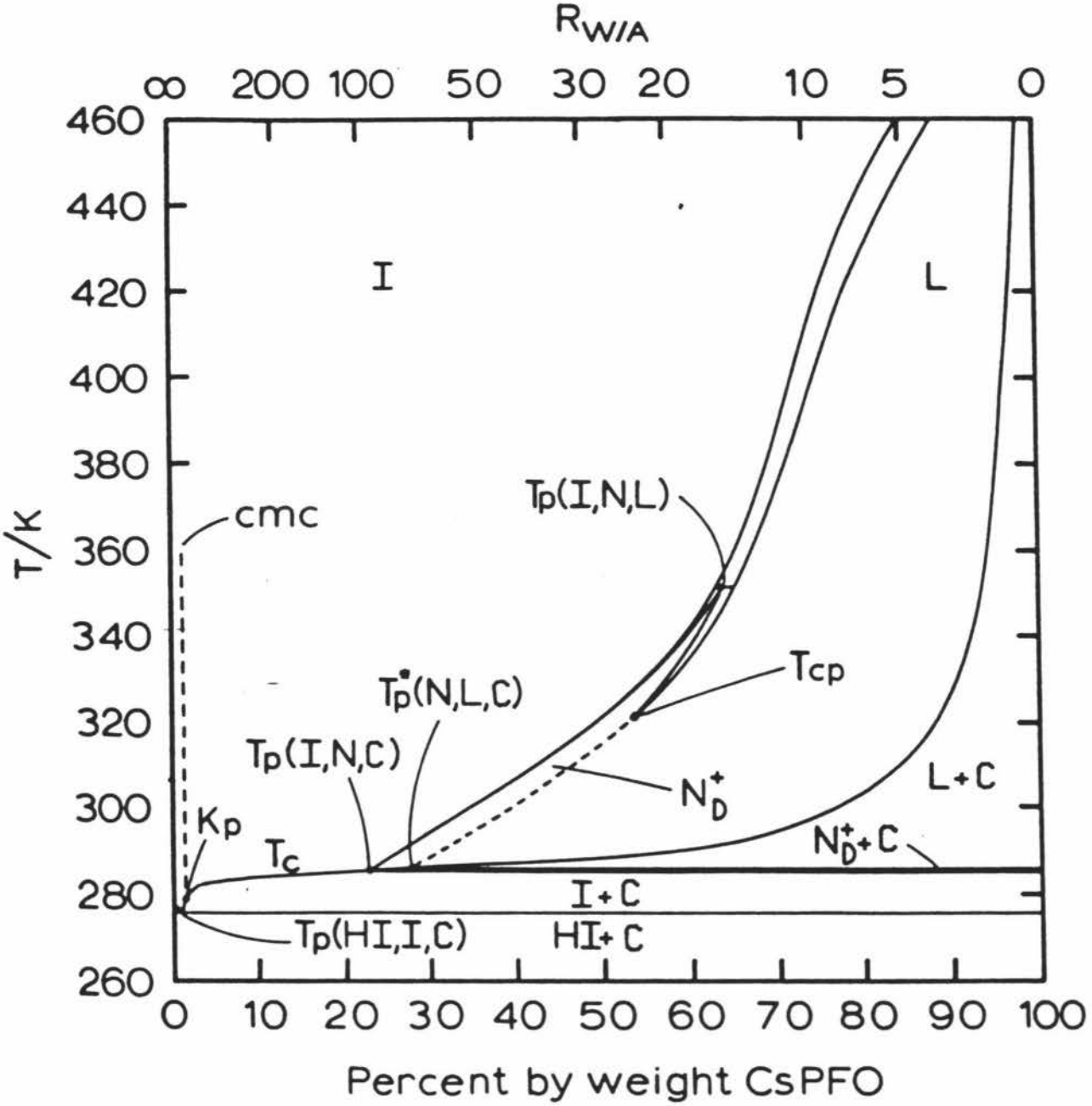
The major impediment to the development of applicable models is the paucity of experimental data about the structures of the aggregates in the various mesophases. For example, the conventional opinion is that lamellar phases consist of bimolecular lamellae of indefinite extent separated by layers of water (neglecting macroscopic structural defects) [7]. Yet, it has recently been suggested [11] that, at least in cases where the lamellar phase gives way to a nematic phase with either increasing temperature or on dilution, the lamellae are actually two dimensional arrays of discoid micelles. An alternative proposal [12] is that the lamellae consist of continuous bimolecular layers (bilayers) penetrated by irregularly shaped `pools' of water and that in the conjugate nematic phase the aggregates are irregularly shaped bilayers. The most likely situation which obtains is that the lamellar phase exists with a variety of structural modifications not unlike the polymorphism of the thermotropic smectic liquid crystals. It is also very probable that the lyotropic columnar phases (hexagonal, tetragonal) will exhibit a wide variety of polymorphism. In the case of the nematic mesophases, it is not known what factors control the size and shape of the micelles and under what conditions these mesophases are thermodynamically stable. A significant and unexpected observation in this context is that in the N_D^+ mesophase of the caesium pentadecafluorooctanoate (CsPFO)/water system the dimensions of the micelles are of the order of the separation of their centres-of-mass, irrespective of amphiphile concentration [13].

Clearly there is a need at present for careful experimental studies of the structure of the amphiphilic aggregates and of the basic physics of the phase transformations for well defined systems which exhibit simple sequences of mesophases such as those referred to above. To explore these phenomena we have embarked on detailed studies of lyotropic liquid crystalline systems.

We have chosen as our model the salts of pentadecafluorooctanoic acid in water. The features that make these systems attractive are as follows. Firstly, fluorinated amphiphiles are much more stable, both chemically and thermally, than hydrocarbon ones. Secondly, they are all simple two component systems. Thirdly, in many systems a nematic phase (N_D^+) occurs over a wide range of concentrations and it is intermediate to a lamellar phase and an isotropic micellar solution, and fourthly, they have a positive diamagnetic anisotropy so that samples with a homeotropic distribution of directors can be prepared. The latter property is of special importance for experimental studies. To our knowledge, there is no other system known to date (apart from the salts of pentadecafluorooctanoic acid and their homologues) which satisfy these requirements.

As a first step in these studies it is vital that accurate phase diagrams be produced. The first system to be studied in detail was the CsPFO/D_2O system a partial phase diagram of limited accuracy for which has been published [14]. Subsequent work undertaken at Leeds and Massey Universities has resulted in a considerable improvement in the resolution of this phase diagram [15]. The refined phase diagram for the CsPFO/D_2O system is shown in Figure 1. The ordinate gives the

Figure 1. The complete phase diagram for the CsPFO/D_2O system. C, crystal; L, lamellar phase; N_D^+, nematic phase with positive diamagnetic anisotropy and discoid micelles; I, isotropic micellar solution; HI, heavy ice. Triple points and other points of interest are as labeled.
From Ref. 15.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$T_p(I,N,C)$
N_D^+
L+C
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T_c
$N_D^+ + C$
I+C
$T_p(HI,I,C)$
HI+C
0 10 20 30 40 50 60 70 80 90 100
Percent by weight CsPFO

temperature and the abscissa the concentration. The latter is given as the percentage by weight of CsPFO on the lower axis and as the mole ratio of water (D_2O) to CsPFO (amphiphile A) $R_{W/A}$ on the top axis. The diagram is unusually simple when compared with those of other amphiphile/water mixtures and shows a number of unique and interesting features.

There are only three homogeneous single phase regions, apart from the pure compounds. These are the isotropic micellar solution, I, (simple molecular solution of amphiphile in water for concentrations less than c.m.c) the nematic phase, N_D^+, and the lamellar phase, L. All of the other areas are two-phase regions in which the system separates into two phases with compositions given by the intersection of horizontal lines (tie-lines) with the phase boundary curves and proportions given by the lever rule. The crystalline CsPFO (C) and heavy ice (HI) are completely immiscible and there is a triple point (eutectic point) Tp(HI,I,C). The curve Tc is the solubility curve for the crystalline amphiphile. The solubility curve meets the c.m.c line at the Krafft point Kp. At higher concentrations, first nematic, then lamellar mesophases are formed. The lamellar phase is unusual for a simple ionic amphiphile in that it occurs over an unusually wide range of concentration. The nematic phase is intermediate to the lamellar and isotropic micellar solution phases and again we see that it exists over an extensive concentration interval; in fact, this is far greater than in any other amphiphile/water system so far reported. For concentrations of amphiphile less than 53.5 weight percent (the composition of an apparent tricritical point, Tcp) the lamellar to nematic phase transition appears to be continuous (i.e no mixed phase

region) suggesting that these transitions are of a higher order than first. It may however simply represent an inability of ^{2}H NMR to distinguish between first and higher order transitions in this region of the phase diagram. This point will be examined in detail in the NMR section of this thesis. The temperature and composition of the various points on the phase diagram are summarised in Table 1.

Table 1. Location of specific points on the CsPFO/D_2O phase diagram.

Point	wt%Amphiphile	Temperature
Tp(I,N,L)	63.0	351.0 K
Tcp	53.5	322.0 K
Tp(I,N,C)	22.5	285.3 K
Tp(N,L,C)	27.5	285.6 K
Kp	1.0	279.0 K
Tp(HI,I,C)	0.9	276.0 K

The purpose of the work presented in this thesis was to investigate the system ammonium pentadecafluorooctanoate/D_2O (APFO/D_2O) as a first step in an investigation into the role of the counter ion in the determination of liquid crystal phase structure and phase transition mechanisms. This system has all the advantages associated with the CsPFO/D_2O system. Previous studies on heptadecafluorononanoate salts [16] suggest that the phase diagram of the ammonium salt should be similar to that of the caesium salt. This study was of a cursory nature however and although a magnetically orientable phase (nematic phase) was identified for the caesium salt no such phase was recognised for the ammonium salt. Hoffmann [17] has recently reported results on

the ammonium heptadecafluorononanoate/D_2O system where a nematic phase was recognised but not fully characterised. This work was later incorporated in another paper which was concerned with the formation of lyotropic liquid crystal mesophases from micellar solutions [18].

Specifically the aim of this work can be divided into two parts.
(1) To map out a high resolution phase diagram for the APFO/D_2O system.
(2) To compare the APFO/D_2O phase diagram with that for the CsPFO/D_2O phase diagram to see if some insight into the role of the counter ion in determining liquid crystal phase structure and phase transition mechanisms could be found.

Experimental

Materials

Ammonium pentadecafluorooctanoate was prepared by the neutralisation of pentadecafluorooctanoic acid (from Koch-Light and Riedel-De Haen) with ammonium hydroxide. The resulting solution was then freeze dried. The APFO thus obtained was recrystallised from a 1:1 butanol/hexane mixture to remove any unreacted acid and then dried under vacuum. No true melting point was established for APFO because it decomposes at 124-128^{o}C The source of the acid used to make the APFO made no difference to any of the measured phase transition temperatures.

NMR

The NMR samples were made by weighing D_2O (Sigma USA ,99.8% ^{2}H) and the APFO directly into 5mm o.d. NMR tubes which were then flame sealed. To avoid losses when the tube is sealed the salt is introduced into the base of the tube through a long glass funnel and the D_2O is added through a long hypodermic syringe needle. The tubes after sealing were placed in an oven at 80^{o}C to equilibrate and were left until they appeared homogeneous.

DSC

For DSC measurements samples were made up into sealed glass vials in the same way as the samples used for NMR. These samples were broken just prior to use then weighed into aluminium pans which were sealed by having their lids crimped in a small press.

Conductivity

A range of weight percent samples from 0.3 to 15 wt% amphiphile were made up by weighing out of a stock 15 wt% amphiphile solution.

Measurements

NMR

Deuterium spectra of D_2O were obtained using a JEOL FX-60 pulse fourier transform NMR. The probe used was originally from a JEOL FX-100. The ^{13}C observation coil of this probe was retuned from 25MHz to the deuterium observation frequency of 9.18MHz. The output signal from this coil was fed into the deuterium lock preamlifier of the probe which was retuned from 15MHz to 9.18MHz. The deuterium lock channel was then used as the observe channel by switching over the lock and observe amplifiers and oscillators on the spectrometer. Field frequency stability was achieved by using an external proton lock (built by C Eccles,Massey). The retuning resulted in a large decrease in the "Q" of the coil and a consequent long $\pi/2$ pulse time of 250 μs. Usually $\pi/4$ pulses were used giving an effective frequency spread of $\pm$2000Hz from the observation pulse frequency which was greater than the range of deuterium frequencies measured in this study. Typically ten repetitions of the $\pi/4$ pulse at 2s intervals were required to produce an adequate signal to noise ratio in the FID. Data were subsequently Fourier transformed using 4000 data points. Sweep widths of 1000Hz were usually used. The temperature control for the system was achieved using a double pass water flow cell (Fig 2) (designed at Leeds University) connected to a Colora WK3 cryostat. This provides temperature control to a precision of $\pm$5 mK.

DSC

The DSC measurements were made using a Perkin-Elmer DSC-2 instrument interfaced with a model 3600 thermal analysis data station which belongs to the Dairy Research Institute, Palmerston North. The DSC was temperature calibrated using a standard indium sample. A schematic

Figure 2. The double pass water flow system used in the NMR experiments.

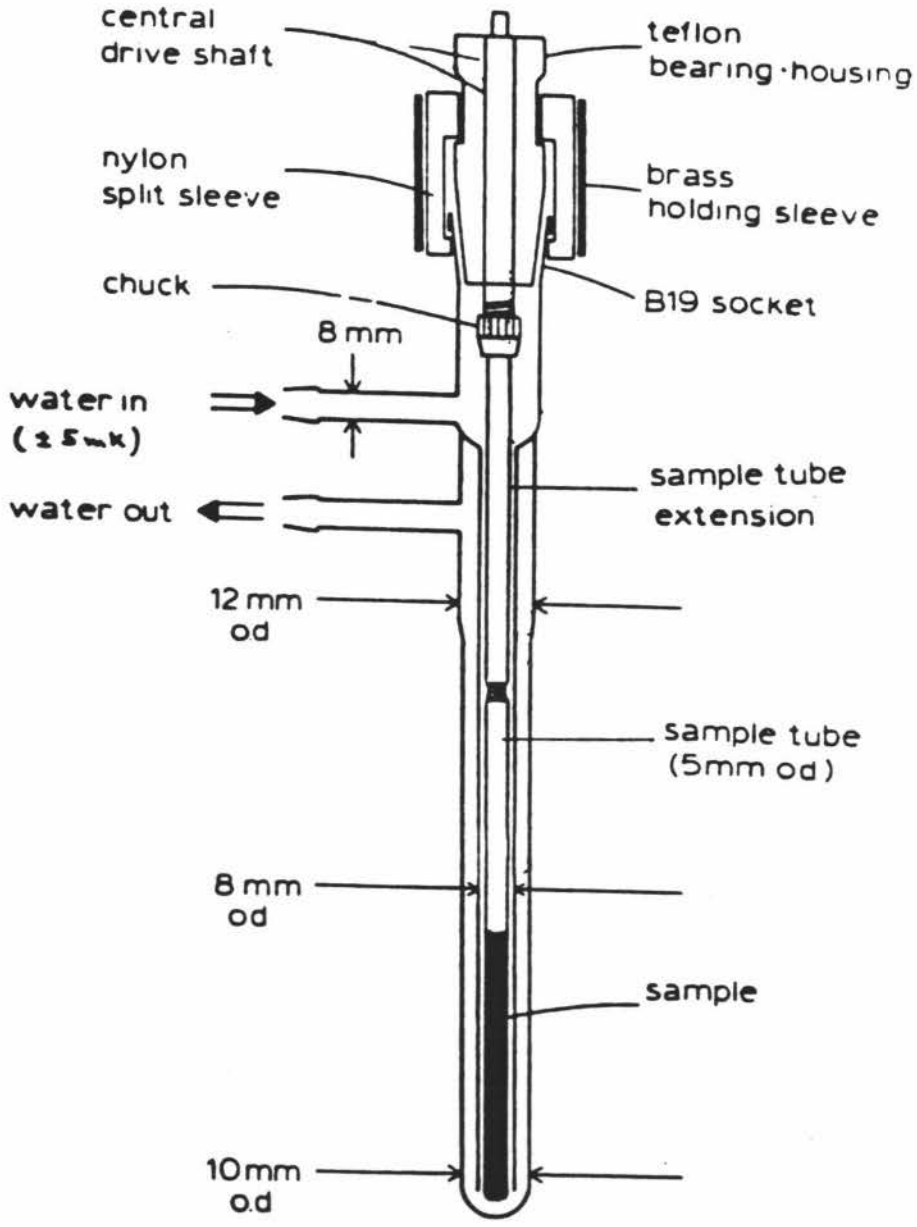
central
drive shaft
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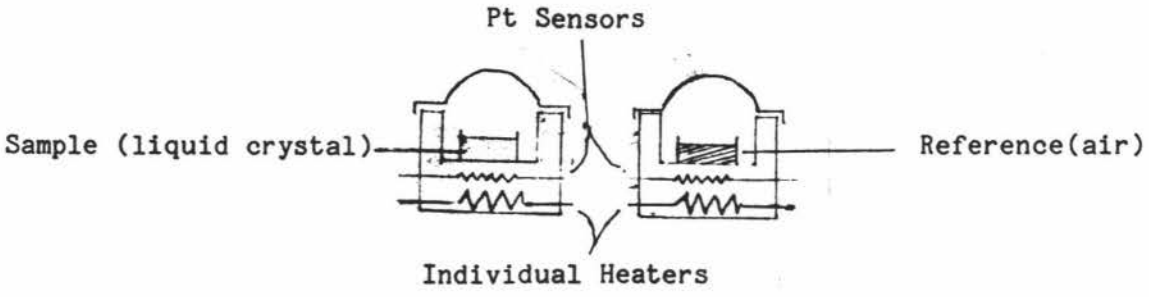
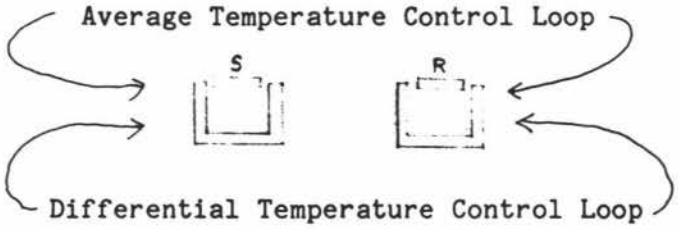
diagram of the instrument is given below.



The DSC can be thought of as having two control loops.



The average temperature control loop enables the temperature of the sample and reference to be increased (or decreased) at a specified rate. The second loop ensures that if a temperature difference develops between the sample and reference , because of an exothermic or endothermic reaction in the sample , the power imput is adjusted to remove this difference. This is known as the null-balance principle. This means that the temperature of the sample holder is always kept the same as that of the reference holder by continuous and automatic adjustment of the heater power. A signal proportional to the difference between the heater input to the sample and that of the reference, dH/dt, is fed into the computer for subsequent analysis.

Conductivity

Conductivity measurements were made using a Phillips PW9509 digital

conductivity meter attached to a Phillips PW9512/61 conductivity cell. A KCl sample of known molality was used to determine the cell constant. The conductivity meter was operated at a frequency of 2000Hz. To regulate the temperature of the sample a double pass water flow system was attached to the outside of the cell (Fig 3) and the Colora Wk3 cryostat was used to control the water temperature to a precisions of $\pm$5 mK , the same as for the NMR experiments.

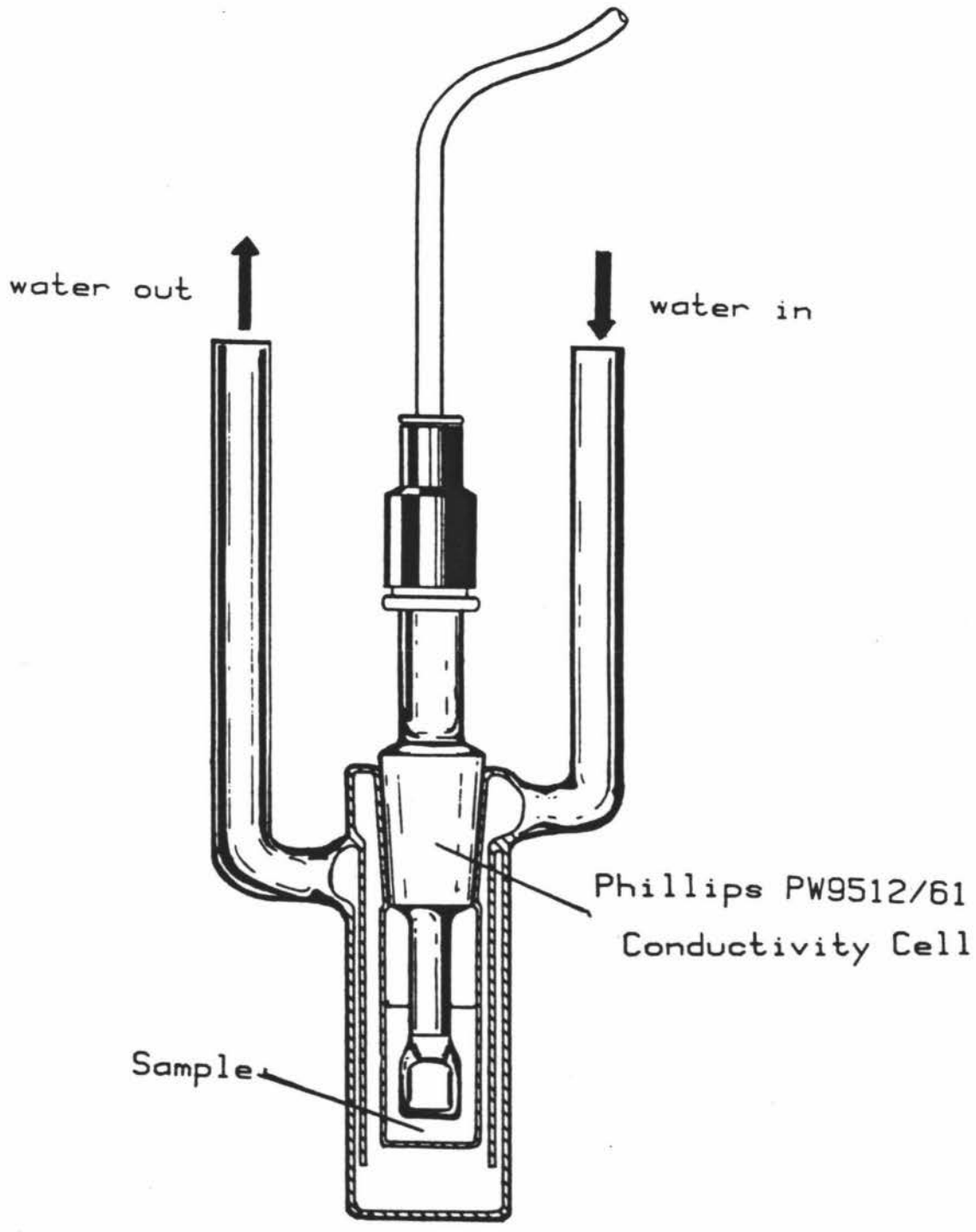
Temperature

All of the temperature measurements for the NMR and conductivity experiments were made using a thermister connected to a Fluke 8050A digital multimeter. The thermister was calibrated against a Hewlett-Packard 2801A digital quartz thermometer coupled with a 2850A temperature probe which had been calibrated at the Physics and Engineering Laboratory of the DSIR in Wellington to an accuracy of 1 mK. The response of the thermister resistance to temperature was accurately represented over small temperature ranges by an Arrhenius expression

$$R = Ae^{B/T}$$

The calibration data was fitted to the above equation and a linear regression performed for the best fit A and B values. The regression coefficients (given in the following table) were then incorporated into a computer program written for the Hewlett-Packard HP85 desk-top computer which calculated the thermodynamic temperature corresponding to any given resistance reading within the calibration range.

Figure 3. The double pass water flow system used in the conductivity experiments.


water out
water in
Phillips PW9512/61
Conductivity Cell
Sample

Calibration Coefficients

T range/K	$Ax10^{5}/k\Omega$	$Bx10^{-3}/K$	r^2
278-293	8.06559	3.11194	0.999996
293-309	7.30319	3.14105	0.999997
309-327	6.80805	3.16291	1.000000
327-348	6.63824	3.17112	0.999999
348-360	6.54938	3.17593	0.999996

r is the coefficient of linear correlation.

The accuracy of the temperatures so measured is $\pm$0.01 K. The high flow rate of the water meant that the temperature of the water entering the sample cell was the same as that leaving the cell within measurement error and therefore ,as expected, it made no difference to the temperature reading if the thermister was in the cell outlet or the cell inlet. This also indicates that the sample resides in a uniform temperature enclosure in which for all practical purposes temperature gradients are absent.

NMR Theory

NMR measurements of the quadrupole splitting of ^2H in labelled water is an unparalleled method for mapping phase diagrams and for studying the mechanism of phase transitions in lyotropic amphiphilic liquid crystals. This is because the quadrupole splitting is a characteristic signature of each kind of phase and is also a function of composition and temperature. It can, therefore, provide detailed information about the uniformity of composition and temperature in bulk samples. This is particularly useful information when traversing two-phase regions as in most instances it enables both the compositions and the relative amounts of the coexisting phases to be monitored. It can also be used to monitor the orientational distribution of the mesophase director in the sample under study and to distinguish between uniaxial and biaxial mesophases. For this reason the NMR theory will be presented in some detail.

The spectrum for ^2H spins (I=1) in labelled water in a macroscopically aligned uniaxial mesophase (nematic , lamellar or hexagonal) is always a symmetric doublet whose quadrupole splitting $\Delta\tilde{\nu}$ is given by

$$\Delta\tilde{\nu} = 3/2\ |\tilde{q}_{zz}|\bar{p}_2 p_2(\cos\Phi) \quad (1)$$

$p_2(\cos\Phi) = 1/3(3\cos^2\Phi - 1)$ where is the angle between the mesophase director $\vec{n}$ and the direction of the magnetic field $\vec{B}$ and $\tilde{q}_{zz}$ is the partially averaged component of the deuterium nuclear quadrupole-electric field coupling measured parallel to the director.

$$\tilde{q}_{zz} = \Sigma p_n \chi_n \{S^n_{cc} + \eta_n(S^n_{aa} - S^n_{bb})\} \quad (2)$$

The S^n_{ij} are the elements of the Saupe ordering matrix for the principle axes (a,b,c) of the nuclear quadrupole coupling interaction tensor at the nth site with statistical weight p_n . $\chi_n = (e^2qQ/h)n$ is the

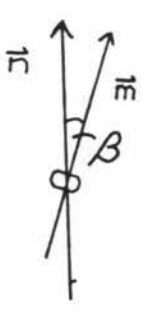
quadrupole coupling constant and η_n is the assymetry parameter. Since for unbound water molecules $\tilde{q}_{zz}$ is zero we have,

$$|\tilde{q}_{zz}| = \frac{n_b x_a}{x_{D_2O}} |\tilde{q}_{zz}|_b \qquad (3)$$

where n_b is the number of water molecules "bound" at the aggregate/water interface (unknown but small) and x_a and x_{D_2O} are the mole fractions of amphiphile and water respectively. $\bar{P}_2$ is a second rank order parameter defined for a monodisperse assembly of micelles by

$$\bar{P}_2 = (3\langle\cos^2\beta\rangle - 1)/2 \qquad (4)$$

where β is the angle between the symmetry axis of the structural units ($\vec{m}$) and the mesophase director ($\vec{n}$) and the angular brackets indicate an ensemble average. For any pure liquid crystal phase $\bar{P}_2$ increases as the temperature decreases as a consquence of the increasing order within the system. A diagramatical representation of the relationship between the vector quantities refered to above, is given in the following figure.

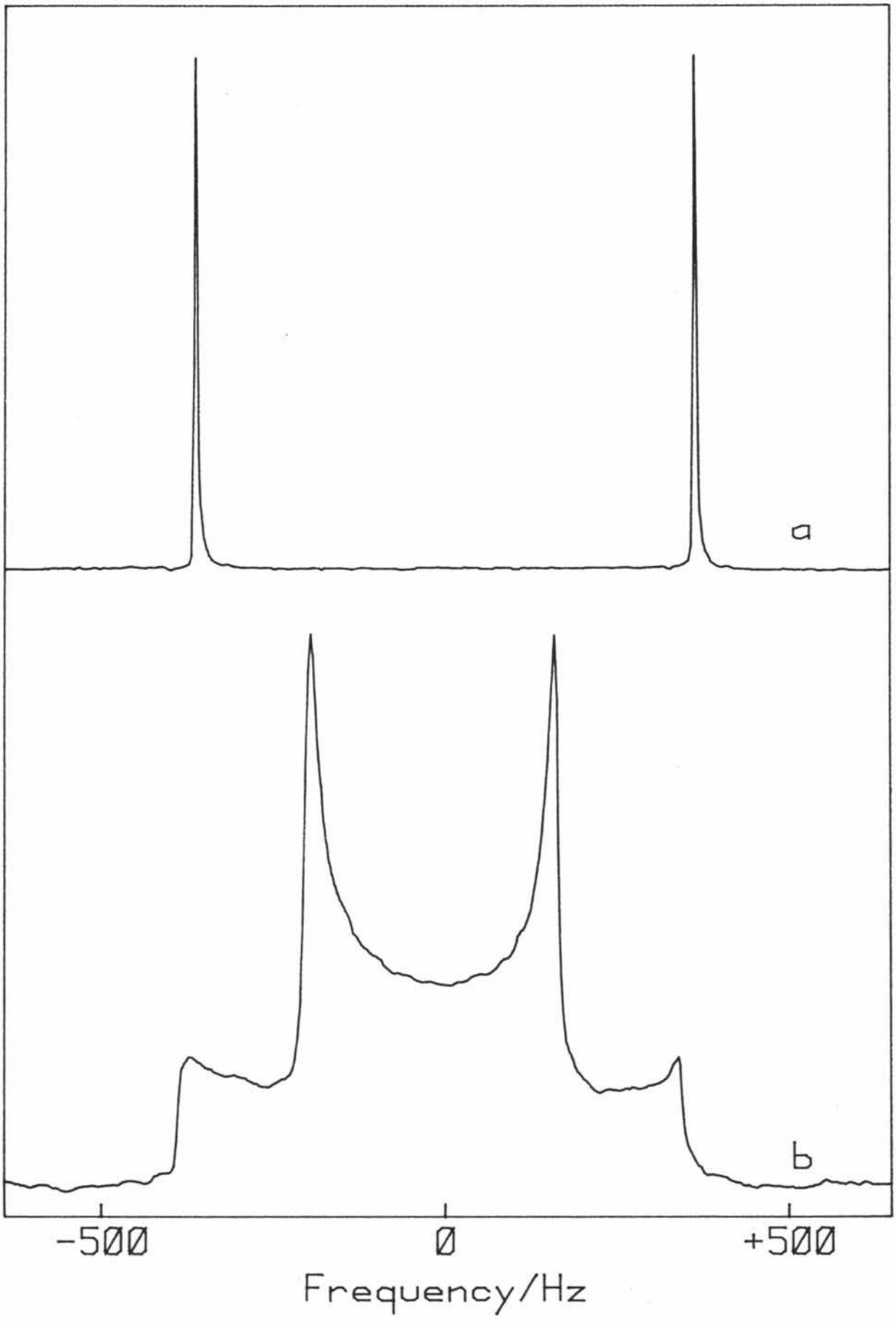


$\bar{P}_2$ will be zero for an isotropic micellar solution and therefore a singlet spectrum is the result. For a nematic mesophase or a lamellar mesophase consisting of two dimensional arrays of discrete discoidal micelles, $0 < \bar{P}_2 < 1$, whereas for the classical lamellar mesophase consisting of infinite bilayers , $\bar{P}_2$ must be equal to one. Both of these lamellar phases will give rise to a doublet spectrum as will the nematic mesophase. The observation of a single doublet implies that motions of the water molecules are fast compared to the experimental time length. The nematic and lamellar mesophases can be distinguished

by their responses to the altering of the position of the mesophase director relative to the spectrometer magnetic field, $\vec{B}$. The nematic mesophase has a finite rotational viscosity coefficient and positive diamagnetic anisotropy and the mesophase director, $\vec{n}$, aligns itself with the magnetic field, $\vec{B}$. Following rotation the sample will realign itself so that its mesophase director, $\vec{n}$, again lies along the direction of the magnetic field , $\vec{B}$. This reorientation takes place in the order of a few seconds over most of the nematic range. and once reorientation is complete and all directors are aligned with $\vec{B}$, a single sharp doublet is again observed. The lamellar phase has a rotational viscosity coefficient of infinite value and therefore the lamellar director is locked into the mesophase and cannot reorientate along $\vec{B}$. After being rotated the spectrum is still a well defined doublet whose splitting is defined by equation (1), i.e $\Delta\tilde{\nu}$ follows a $3\cos^2\Phi-1$ angular dependence. A different spectrum for the lamellar phase is obtained if the sample is cooled outside the magnet instead of inside it. The sample cooled outside the magnet gives a `Pake' spectrum which is consistent with an isotropic director distribution (Fig 4).

The above description refers to a homogeneous (single phase) situation. When two phases are present complications are introduced due to exchange of the D_2O between the phases. For example in a lamellar/nematic mixed phase sample (both doublets) the observation of separate lamellar and nematic doublets is dependent upon the average time a water molecule spends in a particular phase (τ) and the difference in the quadrupole splitting of the two phases ($\delta\Delta\tilde{\nu}$). The doublets will merge when $\tau \approx 1/\pi\delta\Delta\tilde{\nu}$ so that fast exchange (only one

Figure 4. Deuterium NMR spectra of D_2O in the lamellar phase of a 54.21 wt% APFO/D_2O sample with
(a) a homeotropic distrubution of lamellar directors (normals to the planes of the lamellae) and
(b) an isotropic distribution of directors.


a
b
-500
0
+500
Frequency/Hz

doublet which is a weighted average of the nematic and lamellar doublets) implies $\tau < 1/\pi\delta\tilde{\Delta\nu}$ and conversely $\tau > 1/\pi\delta\tilde{\Delta\nu}$ for slow exchange (where the doublets are resolved).

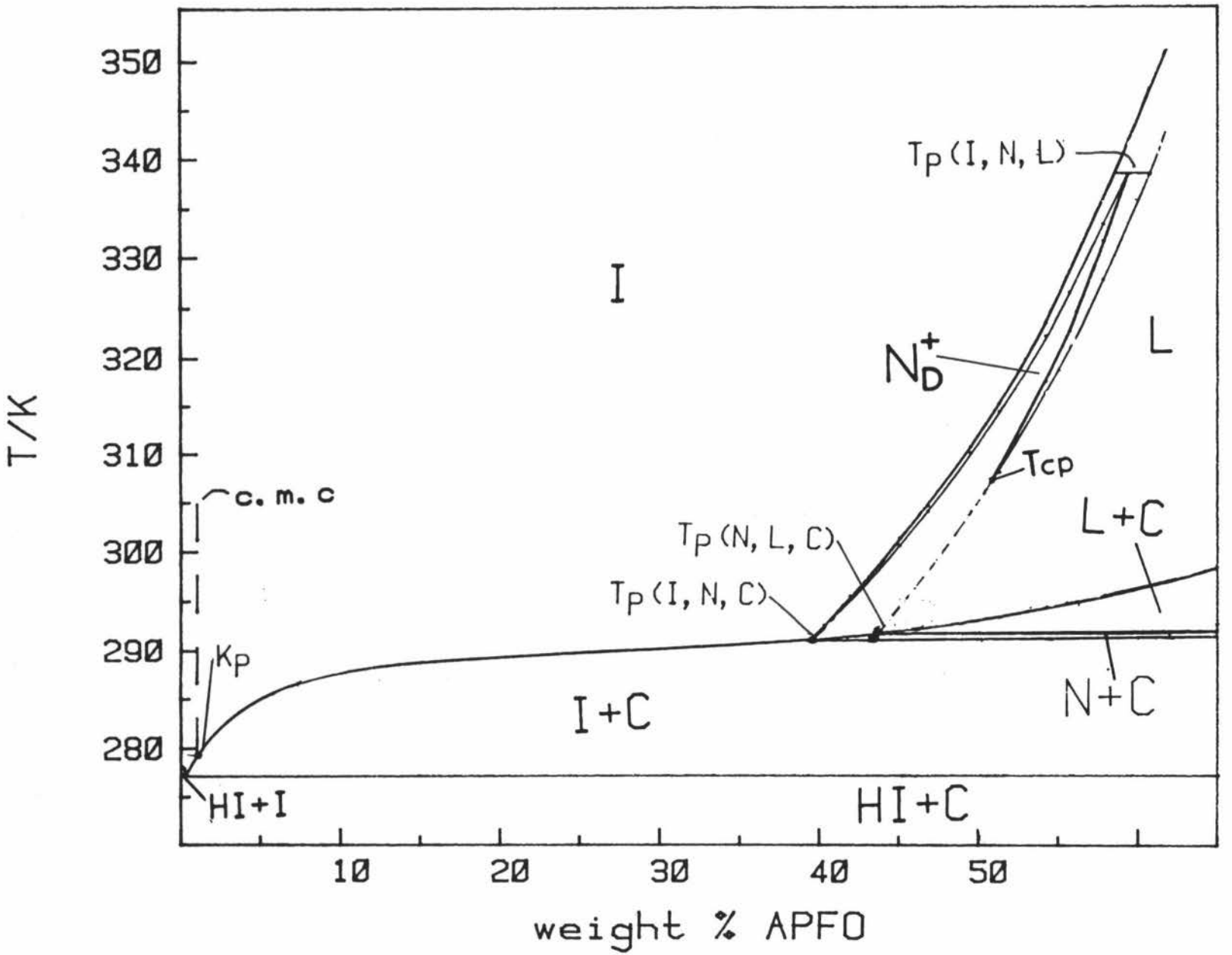
In the case where the mixed phase consists of isotropic (singlet) and either nematic or lamellar (doublets) the fast exchange condition becomes $\tau < 1/(2\pi\tilde{\Delta\nu})$ where $\tilde{\Delta\nu}$ is the quadrupole splitting of the ^2H nucleus of the water in the nematic or lamellar phase domains. In intermediate exchange regions ($\tau \approx 1/(2\pi\tilde{\Delta\nu})$ line broadening will occur. Thus by deuterium NMR we have a means of identifying phases (isotropic, nematic, lamellar) and in favourable situations we can expect to identify mixed phase regions (separate mesophase spectra obtained) and thus in conjunction with the precise and accurate temperature control high resolution phase diagrams can be produced.

Results

The phase diagram for the APFO/D_2O system is given in Fig 5. The ordinate gives the temperature and the abscissa the concentration as weight percent APFO. The ammonium pentadecafluorooctanoate/D_2O system shows an extensive nematic phase over a large range of compositions and temperatures. The nematic phase exists between compositions of 39.6 wt% and 59.6 wt% amphiphile and the temperatures of 291.0 K and 338.4 K. The nematic phase exists up to the isotropic/nematic/lamellar triple point Tp(I,N,L), which occurs at a temperature of 338.4 K. Because the phase transitions in the region of Tp(I,N,L) take place by way of a first order phase transition mechanism the triple point is not a single point but rather a row of points stretching from the isotropic phase boundary to the lamellar phase boundary at the triple point temperature. There is an apparent tricritical point ,Tcp, at an amphiphile composition of 50.8 wt% and at a temperature of 307.2 K. This point is the result of an apparent change from a first order phase transition mechanism to that of a second order mechanism for the lamellar to nematic transition. There is some doubt about the position and even the existence of Tcp and therefore the nematic/lamellar phase boundary between Tcp and the nematic/lamellar/crystalline triple point Tp(N,L,C) is shown on the phase diagram as a dotted line. Tp(N,L,C) is a triple point at which the nematic and lamellar phases exist in the presence of crystalline amphiphile. This fixed point is located at an amphiphile composition of 43.7 wt% and at a temperature of 291.6 K. The other triple point Tp(I,N,C) is located at the position where the isotropic/nematic mixed phase region crosses the solubility curve. Since Tp(I,N,C) is where the three phases coexist ,Tp(I,N,C) is by definition not a single point but a line of points. This line of

Figure 5. A partial phase diagram for the APFO/D_2O system. The symbols used are the same as those used in Fig 1.

The nematic/lamellar transition below Tcp is shown as a dotted line because of uncertainty about the nature of the transition.


350
340
330
320
310
300
290
280
T/K
I
L
N_D^+
T_P (I, N, L)
Tcp
c. m. c
T_P (N, L, C)
T_P (I, N, C)
L+C
K_P
I+C
N+C
HI+I
HI+C
10
20
30
40
50
weight % APFO

points lies on the solubility curve and within the isotropic/nematic mixed phase region. Tp(I,N,C) is therefore located at a temperature of 291.0 K and at a range of compositions between 39.5 wt% and 39.7 wt% amphiphile. The location of the triple points Tp(I,N,C) and Tp(N,L,C) was facilitated by the fact that the APFO/D_2O system (and the CsPFO/D_2O system) produces supercooled liquid crystal mesophases and so the T_{IN},T_{NI} and T_{NL} curves could be extended below Tc. The intersection of these curves with Tc gave the location of the triple points. Another unique point in this system is the eutectic point. At this point the solution and both solid phases coexist i.e. heavy ice, crystal and isotropic solution. This eutectic point occurs at a temperature of 277.0 K and at a composition of 0.4 wt%. The Krafft point occurs at a concentration of 1.1 wt% and a temperature of 279.2 K. The Krafft point is the point where the c.m.c intersects the solubility curve. To the left of the c.m.c curve the isotropic solution is molecular and to the right of it the solution is isotropic micellar.

All the phases have been marked out by using experimental data except for the nematic/crystalline region. This region is intuitive and has been included because the positioning of the Tp(I,N,C) and Tp(N,L,C) triple points at slightly different temperatures demands the inclusion of a nematic/crystalline region. If these triple points were at the same temperature it would imply that all four phases coexisted ,which is not possible and therefore to prevent the meeting of the four phases a narrow nematic/lamellar region is postulated. The temperature and composition of the various points on the APFO/D_2O phase diagram are summarised in Table 2.

Table 2. Location of specific points on the AFFO/D_2O phase diagram

Point	wt%Amphiphile	Temperature
Tp(I,N,L)	59.6	338.4 K
Tcp	50.8	307.1 K
Tp(I,N,C)	39.6	291.0 K
Tp(N,L,C)	43.7	291.6 K
Kp	1.1	279.2 K
Tp(HI,I,C)	0.4	277.0 K

NMR

The phase boundaries T_{IN} ,T_{NI} ,T_{NL} ,T_{LN} ,T_{IL} and T_{LI} have all been determined by deuterium NMR and are defined as follows

T_{IN} - The upper limit of the isotropic/nematic mixed phase region

T_{NI} - The lower limit of the isotropic/nematic mixed phase region

T_{NL} - The upper limit of the nematic/lamellar mixed phase region

T_{LN} - The lower limit of the nematic/lamellar mixed phase region

T_{IL} - The upper limit of the isotropic/lamellar mixed phase region

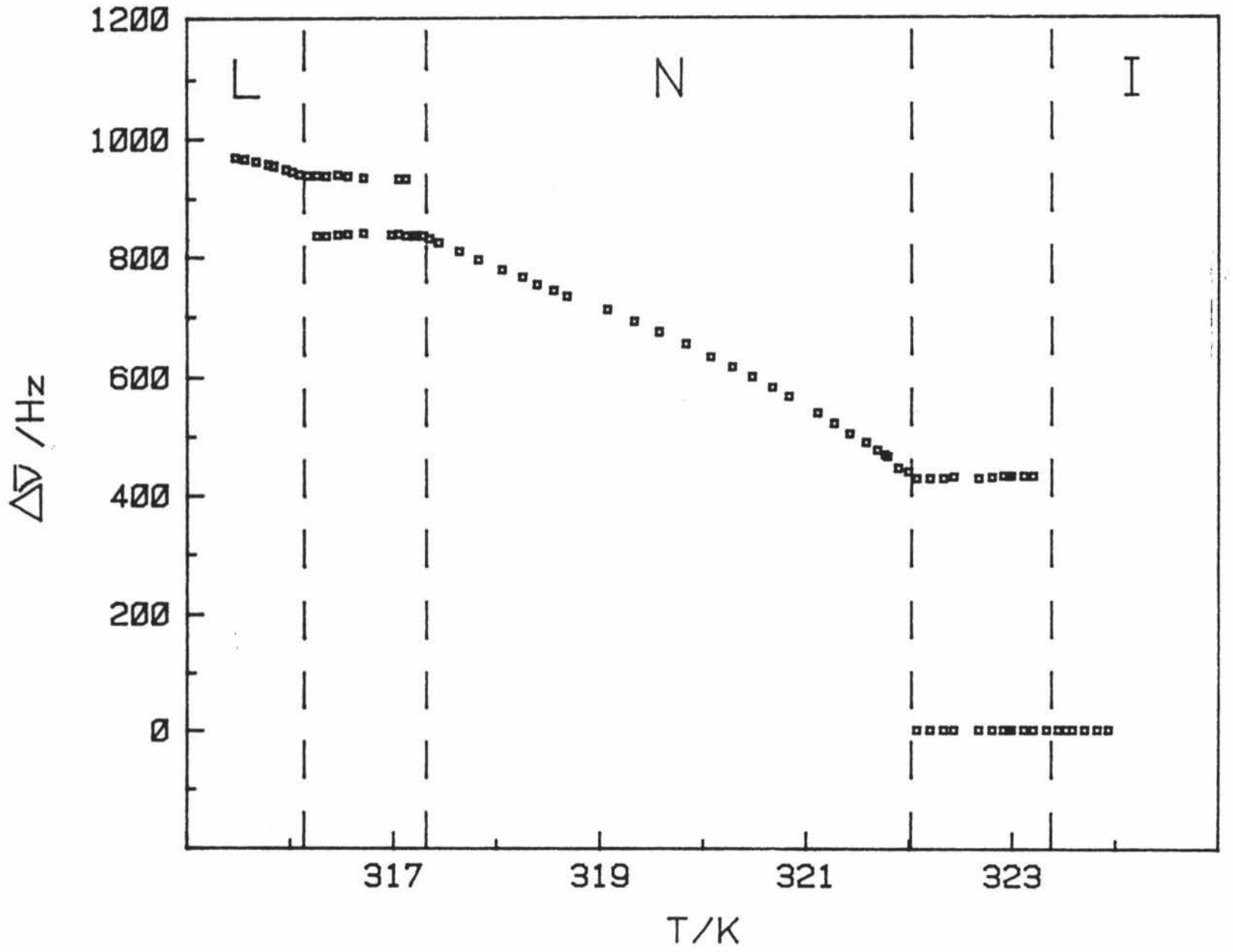
T_{LI} - The lower limit of the isotropic/lamellar mixed phase region

Before discussing the detailed NMR observations on crossing phase transition boundaries it is instructive to consider the temperature dependence of the quadrupole splitting ($\Delta\tilde{\nu}$) on passing from isotropic to lamellar phase via the nematic phase. There are two types of $\Delta\tilde{\nu}/T$ curves depending on the amphiphile composition. At compositions greater that 51 wt percent APFO separate nematic and lamellar doublets are observed on crossing the nematic/lamellar mixed phase region, whilst below this composition only one doublet is seen. The high amphiphile composition behaviour is illustrated by the 54.21 wt percent

APFO sample as shown in Fig 6.

In the isotropic phase $\tilde{\Delta\nu}$ is equal to zero therefore the spectrum is a singlet. On cooling along the 54.21 wt% isopleth, once T_{IN} is reached a doublet starts to form (as the nematic phase forms $\bar{P}_2>0$, eq 1) and on further cooling the doublet intensity increases at the expense of the intensity of the singlet. The change in the relative amounts of the two phases within the mixed N/I region is consistent with the lever rule and the composition of the two phases can be read from the phase diagram using a horizontal line which intersects the sample composition and the sample temperature. The quadrupole splitting remains constant (to a first approximation) as the temperature is decreased through the mixed phase region due to a fortuitous balancing of temperature effects on $\bar{P}_2$ and $|\tilde{q}_{zz}|$ (equation 1). As the temperature is decreased $\bar{P}_2$ increases and this is balanced by the decrease in $|\tilde{q}_{zz}|$ (eq.3) as a result of the decreasing amphiphile composition of the nematic phase. There is an increase in $\tilde{\Delta\nu}$ as the cooling continues through the pure nematic phase as a consequence of the increase in $\bar{P}_2$. At T_{NL} a discontinuity in $\tilde{\Delta\nu}$ occurs which is accompanied by the appearance of separate nematic and lamellar doublets. This is because within the mixed N/L phase region there is a difference in both $\bar{P}_2$ and $|\tilde{q}_{zz}|$ between the nematic and lamellar phases. These differences are small for the systems we have studied and therefore we can assume that there is no fundamental change in micelle structure as the phase change occurs. The $\tilde{\Delta\nu}$ values for the nematic and lamellar doublets are again fairly constant across the N/L mixed phase region for the same reasons as for the isotropic/nematic mixed phase region. In the lamellar phase $\tilde{\Delta\nu}$ gradually increases with decreasing temperature because of the

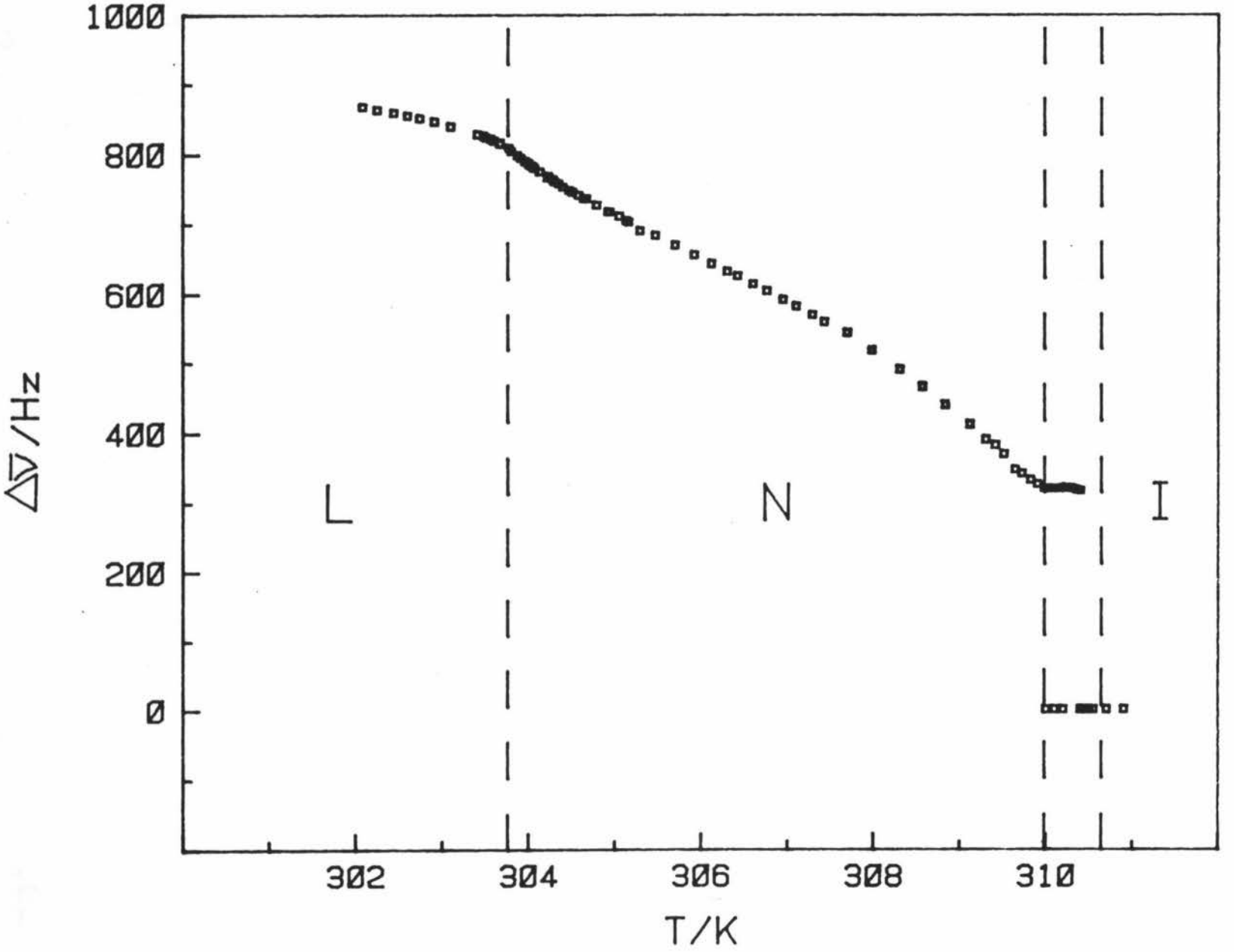
Figure 6. Partially averaged quadrupole splitting of D_2O as observed on cooling through the isotropic to nematic and nematic to lamellar transitions in a 54.21 wt% APFO/D_2O sample. Identical behaviour is observed on heating from the ordered lamellar phase to the isotropic micellar phase. Note that the splitting changes discontinuously at the lamellar to nematic transition where it is first order.


1200
1000
800
600
400
200
0
Δν /Hz
L
N
I
317
319
321
323
T/K

gradual increase in $\bar{p}_2$.

For compositions below Tcp no discontinuity occurs in $\Delta\tilde{\nu}$ but a discontinuity in the temperature dependence of $\Delta\tilde{\nu}$ does occur (Fig 7).

Figure 7. Partially averaged quadrupole splitting of D_2O as observed on cooling through the isotropic to nematic and nematic to lamellar transitions in a 49.50 wt% APFO/D_2O sample. Identical behaviour is observed on heating from the ordered lamellar phase to the isotropic micellar phase. Note that the splitting is continuous across the lamellar to nematic transition but that there is a discontinuity in the temperature dependence of splitting. This is due either to the transition being second order or to it being weakly first order.


1000
800
600
400
200
0
Δν̄/Hz
L
N
I
302
304
306
308
310
T/K